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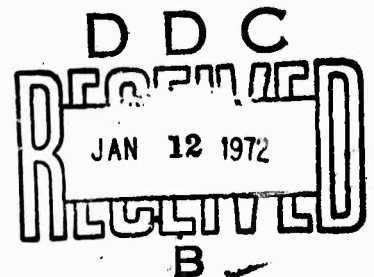
**RADIATIVE BEHAVIOR OF METAL OXIDES IN
LASER BLOWOFF**

**Final Report
9 May 1971**

By

**Tunis Wentink, Jr., Principal Investigator
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REPORT SUMMARY

or

ABSTRACT

Radiative lifetimes of selected molecular and atomic levels were measured in the vapor produced by laser blowoff; i. e., by pulsed vaporization of solid targets in vacuum, illuminated by focused laser radiation. AlO, FeO, C₂, Al, Li, and U spectra so produced were recorded, and AlO, Al, C₂, and Li lifetimes were measured.

The AlO A-X band system absolute intensity constants obtained are in good agreement with recent theory. The corresponding experimental lifetime of the 0, 0 band (272 ns) seems validated by extensive check measurements on a C₂ swan band and a selected Li line. Results on two other Li lines can be explained by expected cascading, and are reasonable. However, the results on Al need further study and explanation.

A search for UO characteristic spectra in the 3100-6400⁸Å region was made, using U, UO₂, and U+UO₂ targets excited in high vacuum or in inert, oxidizing, and reducing atmospheres. Rich spectra were recorded, but only lines and/or continua were found.

Recommendations for future work are made.

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I. INTRODUCTION

A. OBJECTIVE

The spectroscopy and emission-time behavior of metal oxides in laser-induced blowoff were to be studied, experimentally and analytically. Absolute intensity radiation constants, such as level lifetimes, and survey and refinement of molecular potential well constants were objectives. The diatomic AlO and FeO were priority candidate molecules.

B. PROGRAM

This final report is written along the lines spelled out in the original proposal work statement, which is given below. Panametrics proposed a thirteen month program of experimental research and analysis on the behavior of molecular oxide radiation excited in the laser blowoff. Aluminum and iron oxides were to be stressed. The entire program is unclassified. The work was to consist of ten months of experiments and analysis, followed by a one month period for drafting the final report, and then revision, final approval, and distribution of that report in the last two months. Actually, experimental work was continued through much of the scheduled reporting and revision period, since the basic laser blowoff study is the doctoral thesis subject of one of the program participants (G. Diebold, of Panametrics and Boston College).

Work Statement

Panametrics will do the following:

1. Using ruby laser-induced blowoff from selected targets, measure the radiative lifetimes of selected bands of AlO (aluminum monoxide). Do this as a function of laser flux (on target) and ambient pressure above the target.
 - (a) From the spontaneous radiative lifetimes and known molecular constants deduce the corresponding f-values and transition moments of AlO.

2. As in (1) above, examine the spectra and lifetimes of the FeO molecule.
 - (a) From all available spectral data deduce the best values of molecular constants (like ω_e) for identifiable FeO states.
 - (b) Dependent on the final quality of the molecular constants, carry out a parametric analysis of the probable range of Franck-Condon factors of various FeO transitions.
 - (c) From measured radiative lifetimes and results of (2b) above deduce the probable range of f-values and transition moments of FeO transitions.
3. As results and time permit, extend the procedure of (1) and (2) to studies of LiO and other molecules, after discussion with the contract monitor.
4. Write a Final Report on the above, with emphasis on utility of the data to infer behavior of the electronic ground state, and infrared radiation from metal oxide diatomic molecules. Also prepare a comprehensive survey of metallic oxide absolute intensity constants. Pay particular attention to resolution of known discrepancies in past AlO work. Do same for other molecules.

C. APPROACH TO THE PROBLEM

The important fact in the following is that absolute intensity data can be obtained from measurement of the spontaneous radiative lifetime of a level. Only decay rates need measurement, and the data reduction is independent of knowledge of specie concentration. This latter point is a well known and formidable problem, especially when dealing with low volatility refractory materials like AlO.

Implicit through this program is the fact we deal with excited electronic molecular states, but seek to obtain information pertinent to predicting behavior of the ground electronic state.

1. Absolute Intensity Constants

The absolute emission intensity of a molecular band $I_{\nu' \nu''}$, from a source of fixed geometry (size, distance, particle density, etc.) characterized by a constant k_o , and a measured intensity I_m is given by

$$I_m k_o = I_{\nu' \nu''} = KN_{\nu'} R_{\nu' \nu''}^2 \nu_{\nu' \nu''}^3 q_{\nu' \nu''}^4$$

where K involves basic constants. Recall $I_{\nu' \nu''} = N_{\nu'} h\nu A_{\nu' \nu''}$.

In the following analysis the following additional equations were used

$$\frac{1}{\tau_{\nu'}} = \frac{64\pi^4}{3hg_n} \sum_{\nu''=0}^{\nu''=\max} \nu_{\nu' \nu''}^3 q_{\nu' \nu''}^3 R_{\nu' \nu''}^2$$

$$f_{mn\nu' \nu''} = \frac{8\pi^2 m_e c}{3he^2 g_m} \nu_{\nu' \nu''} q_{\nu' \nu''}^3 R_{\nu' \nu''}^2$$

$$f_{nm\nu' \nu''} = \frac{g_m}{g_n} f_{mn\nu' \nu''}$$

$$A_{\nu' \nu''} = \frac{64\pi^4}{3hg_n} q_{\nu' \nu''}^3 \nu_{\nu' \nu''}^3 R_{\nu' \nu''}^2$$

$$\frac{1}{\tau_{\nu'}} = \sum_{\nu''} A_{\nu' \nu''}$$

where h , m_e , e and c are the well known basic constants,

$\nu_{\nu' \nu''}$ is the wave number of the band origin,

v' and v'' are the vibrational quantum numbers of the upper and lower states, respectively,
 g_n and g_m are the total electronic degeneracies of the upper and lower electronic states, respectively,
 $q_{v'v''}$ is the Franck-Condon factor,
 $R_{v'v''}$ is the electronic transition moment,
 $\tau_{v'}$ is the radiative lifetime (spontaneous) of the v' level,
 $f_{mnv'v''}$ is the band oscillator strength (f-value) in absorption,
 $f_{nmv'v''}$ is the band oscillator strength (f-value) in emission,
 $A_{v'v''}$ is the Einstein spontaneous transition probability, and
 $N_{v'}$ is the population of the v' level.

D. LITERATURE SURVEYS

Two separate literature surveys were made during this reporting period, based on extensive surveys made in earlier works by us.^{1,2} One survey dealt with the spectroscopic characteristics of the molecules of chief concern. Resulting brief reviews on AlO and FeO are given below. The latter is treated in more detail in Appendix I. A survey on BaO is also described later.

A separate survey dealt with the production and characterization of the laser-induced blowoff from solid targets. This literature is marked by emphasis on the production and behavior of electrons and ions in the blowoff and the comparatively sparse knowledge of neutral particles in the blowoff. It is this latter area of relative ignorance with which we are concerned, and to which we return later in this report.

1. Status of AlO

The intense aluminum oxide band system ($A^2\Sigma - X^2\Sigma$) in the blue-green has been extensively studied. It apparently is well characterized spectroscopically in all respects, excepting the absolute intensity constants. For the latter, despite much and careful work, there are considerable differences. See Table I.

While there still are not excellent cross checks among different methods, the results of Vanpee, et al³ from flames and those by Hooker and Main⁴ from a shock tube overlap. The former gave, for instance, f_{mn00} with a claimed $\pm 80\%$ uncertainty, while the latter assign $\pm 30\%$ uncertainty to their measure of the same $f_{mnv'v''}$. The shock tube results of Wurster⁵ (Cornell Aero Lab) are thought to be anomalously high, but despite careful scrutiny for errors remain unexplained and not changed appreciably.

However, a very recent theoretical calculation by Michels, et al⁶ leads to an f -value appreciably greater than those of references 3 or 4. Hence, since either the thermodynamics involved in data reduction in the experimental works or the complex nature of the theoretical calculations can lead to considerable uncertainties, more inputs are needed. Thus, an experimental level lifetime measurement, which is independent of concentrations and knowledge of complex electronic wave functions, is expected to help resolve the discrepancies.

As noted in Table I and as we describe later, the laser blowoff results, while needing more substantiation, are in excellent agreement with the theoretical value. The flame, most shock tube, laser and best theoretical estimates have a maximum spread of about 3.5 (i.e., band f from 1.0(-2) to 3.5(-3)).

2. Status of FeO

While strong bands of FeO ranging from the blue to the near infrared are encountered in many sources (arcs, flames, reentry bodies), the spectroscopy is far from resolved. There are at least 4 band systems, A, B, C, and D (Infrared) systems, with many bands measured. However, none of the excited electronic states seem to have been definitely assigned as to configuration. Even the ground state is uncertain, but probably is a $^5\Sigma$ or $^7\Sigma$ state.⁷ Similarly, the internuclear distances of the various excited states are not established to any precision. We know of no absolute intensity data.

Table I

Absolute Intensity Constants of AlO (A-X)

<u>Data Source (Ref.)</u>	<u>Method</u>	<u>Band</u> $f_{mn}^{**} v^I v^{II}$	<u>System*</u> f_{mn} at 0, 0	$\tau_{v^I} \mu s$	R_e, D
Thiokol (3)	Flame (CN-O ₂ -TMA)	2.7(-3)	3.7(-3)	1.00	0.87
Cornell Aero (5)	Shock Tube	1.3(-1)	1.8(-1)	0.02	5.1 (!)
Australian WRE	Grenade- Glow Cloud	5(-3)	-	-	-
United/AFWL (6)	Theoretical	1.2(-2)	1.6(-2)	0.23	1.81
KMS Tech. (4)	Shock Tube	3.5(-3)	4.8(-3) [†]	0.77	-
Panametrics	Estimated, for scaling	3.55(-3)	4.9(-3)	0.76	1.00***
Panametrics	Laser, Blowoff	1.0(-2)	1.4(-2)	0.27	-

(-n) = 10⁻ⁿ multiplier.

$$*f_{mn}(\text{system, at } 0, 0) \approx \frac{f_{mn00}}{q_{00}} \text{ where } q_{00} = 0.730.$$

[†]Note our system f_{mn} is not the definition accepted in ref. 4.

** $v^I, v^{II} = 0, 0$

*** Assigned value, for estimation of τ and f -values.

The above leads to the lamentable fact that, while the abundance and strength of the transitions should permit recording of spectra and measurement of radiative lifetimes, reduction of these data will require approximations. Thus, level degeneracies must be assumed, and a parametric study of Franck-Condon factors using a range of internuclear distances must be carried out. Then, even with known radiative lifetimes, there will be for the present an uncertainty in the f -values.

Of course, knowledge of radiative lifetimes may be useful in influencing other studies on FeO. Also, expected eventual progress in assembling the electronic state level diagram for FeO will permit refining the f -values. As part of this program we sought to accumulate all known data to construct the most up-to-date level diagram for FeO. Results to date are contained in Appendix I to this report.

II. EXPERIMENTAL APPROACH

A. LASER BLOWOFF

The experimental method we employ has been described often in the literature. In short, laser ruby pulses focused on or near a solid target are the heat source, and radiative decays in the target vapor are measured after termination of the laser pulse. A major problem (for our purposes) is the requirement to work near threshold of radiation damage, to minimize further vapor absorption and heating, and destruction of the vapor molecules,

1. The Blowoff Literature

Instead of listing the voluminous bibliography we have accumulated, it seems most efficient to quote the excellent review paper and accompanying extensive (212 references, through 1968) of DeMichelis⁸ on the subject of laser interaction with solids. An especially good paper is that of Basov, et al.⁹ With a few exceptions discussed below, the main effort since the start of 1963 seems to have been on the production of high temperature highly ionized plasmas. The diagnostic detectors of the blowoff were applied mostly to the ionization and electron behavior. Few works covered spectroscopy, especially of neutrals like normal molecules. Apparently Jeunehomme and Schwenker^(8 - his ref. 130) were the first to report radiative lifetimes (for C₂ Swan) deduced from laser blowoff experiments. Wentink, et al^{1,2} have studied in this way band systems of C₂, SiO, VO, and BaO. See Table 5 presented later.

2. Experimental Technique

A sketch of the experimental equipment is given in Fig. 1 (reproduced from Ref. 2). The ruby laser (see Acknowledgments) was an Applied Lasers, Inc. unit, corresponding, after company reorganization, to a Spaceraes, Inc. Model 1010c2; the ruby rod used was 6-1/4" x 5/8" diameter. It was Q-switched variously by a rotating mirror and cyanine dye in combination, or by the dye alone.

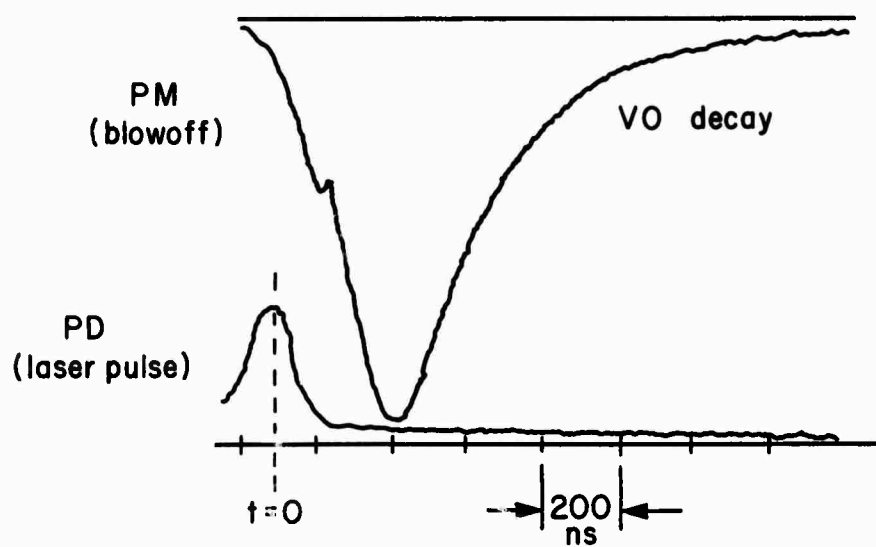
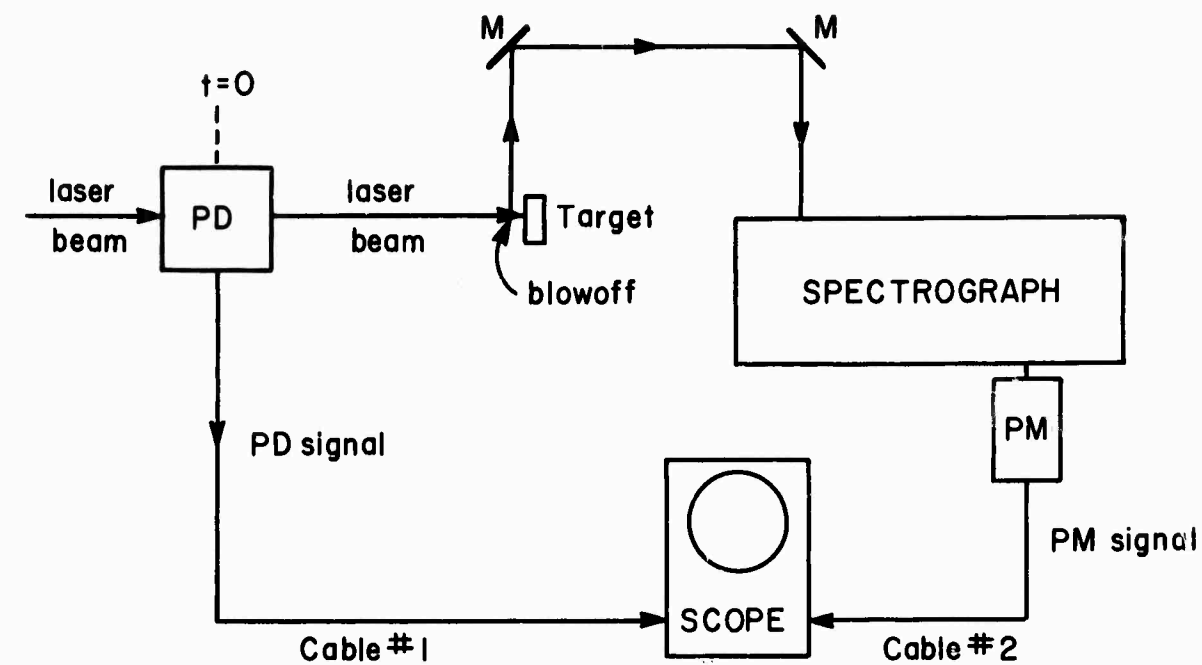


Figure 1. Delay paths in Laser Blowoff Experiment and Typical Signal Presentation. (Polaroid tracing).

The laser burst usually employed, using only the dye switching, consisted of 3 to 5 pulses, each near 80 nsec half-width and spaced about 30 μ sec. These pulses were far enough apart so that each shot in effect gave 3 to 5 blowoff experimental data on each Polaroid film used for recording. See Ref. 8 - his Ref. 179, for a description of the rapid temperature variations during laser-induced heating and vaporization. The unusually long laser pulse width is the major limitation on the lifetime resolution capability.

The measured divergence of the output beam was ~ 7 milliradian full angle. For various reasons two different optical systems were used to focus the beam on the target. The one usually used employed a simple glass lens of measured 50 cm focal length. Apparently the laser beam divergence was sufficient to dictate best focus on target at 56 cm. This lens was outside a Pyrex vacuum (10^{-3} to 10^{-5} torr) chamber containing the target. The chamber input and exit windows were quartz. Another input optical system used consisted of several glass lenses to spread, then collimate the beam, and finally to bring the beam to a very small spot (less than 1 mm diameter) on the target. In this case the last, short focal length lens was inside the chamber, near the target. It is this system that was used mostly in the experiments on the Al plated fibers and thin films described later.

Target vapor ($T \sim 2-4000^\circ\text{K}$)⁸ radiation was collected initially in the program through plane and spherical mirrors which effectively transferred the spectrograph slit to a position a few mm off the target surface. A Dove prism was inserted in the exit optical train to rotate the slit position 90° so as to be perpendicular to the target surface. Later we replaced this cumbersome and not too satisfactory system with a simple glass lens and rotated the spectrograph slit 90° by turning the instrument on its side.

Spectra were recorded mostly with Polaroid film to verify the bands to be studied. Then specific bands were isolated spectrally and their

intensity decays monitored by converting the spectrograph to a monochromator, using a slit and photomultiplier at the spectrograph exit focal plane. The spectrographs were specially constructed Czerney-Turner units, f/7 aperture, of 66 cm focal length. The reciprocal dispersion was $23\text{\AA}/\text{mm}$ in first order for one spectrograph, and $10\text{\AA}/\text{mm}$ in first order in another.

Pulse peak powers and shapes were measured and monitored for each laser shot, using a photodiode unit of well known design. A beam splitter (thin clear glass plates) diverts a small portion of the ruby pulse through heavily attenuating "neutral" density ($D = 1.0$ or 2.0) filters and opal glass onto a United Detector Technology 0.5" diameter PIN-photodiode (S-1 spectral sensitivity). The calibration described here applies to $D = 2.0$. Data recording is oscillographic. The monitor pulses appear on the same picture as do the photomultiplier decay outputs. Thanks to the close cooperation and active assistance of Dr. H. Furumoto and H. Ceccon of NASA-ERC, the absolute calibration of our device was made by comparison with an EG&G Model 580 Radiometer. Typical resulting calibrations gave 12.3 MW (peak) per volt scope deflection. In our experiments reported here we worked usually in the 1 to 5 MW/pulse peak power range.

The above is applicable to all but the survey experiments on uranium-containing targets we describe later. It was necessary late in the program to replace the PIN-photodiode, and we also lost access to the EG&G radiometer. Thus in the U-UO section we note instead of power levels, the voltage peak of the new photodiode and whether the associated neutral density filter was of density 1.0 or 2.0. This can be related roughly to the original calibration, but we prefer to note only changes in laser power level. Recalibration and cross-checks were intended in the follow-on program, but this did not materialize.

B. VALIDITY OF THE METHOD

In any radiative lifetime work there are many questions concerning extraction of the desired fundamental constants from the recorded data. Then there is the more important question of how meaningful are the results obtained from the laser blowoff technique?

We reserve detailed treatment of the latter question for the Discussion (Section IV). The short answer is that empirically the method seems to give reasonable and often good agreement with experimental results from vastly different techniques, like shock tube emission or absorption measurements. When checks are possible, the lifetimes from the laser blowoff usually are longer than from other methods, but in the poorer cases still within a factor of 2 or 3. We cannot comment on this more, since predictions through theoretical treatment of the blowoff are complex. We do note there is need for more analytical theory about the behavior of neutral particles near threshold of blowoff. See Section V on Recommendations, and recall I-D and II-A-1.

Returning to the question of raw data processing, the signals, if weak, are often noisy, and are limited in dynamic range if data recording is by the usual Polaroid recording of the fast one-shot oscilloscopic displays. Then first semi-log plots of the data may indicate more than one exponential present. This problem is characteristic of lifetime studies, and not peculiar to the blowoff approach. Some measure of the inherent limitations of the graphical treatment of multiple exponential behavior is illustrated thus: We computed and plotted an artificial signal, applicable to the Li case described in III-B:

$$E_{\text{sig}} = 10 e^{-t/\tau_1} + 1.70 e^{-t/\tau_2}$$

where $\tau_1 = 65 \text{ ns}$ and $\tau_2 = 242 \text{ ns}$.

The careful semilog plot of this noise-free synthetic signal yielded from the two major graphical slopes apparent $\tau_1 = 81$ ns and $\tau_2 = 223$ ns. Removing the second component (at 223 ns) from the total gave a refined $\tau_1 = 61$ ns (vs the input 65 ns). In dealing with experimental data that contains more than one exponential it is usually necessary to get at least two decades of dynamic range in the signal, sufficient signal-to-noise to minimize noise and get at least 2 significant figures in most data points. Often computer processing to extract reasonably precise τ s from the experimental data is necessary, unless the various τ s are appreciably different. This problem is treated more in reference 1 and references therein.

III. RESULTS

Chronologically, the experimental program started with survey spectra on AlO and FeO, then lifetime measurements on AlO, followed by checks for lifetime system calibration using the C_2 Swan bands, attempted use of Al lines for further calibration, considerable study of the Al lines, and then lifetime measurements in Li (LiI spectra) for further system calibration and validation. Finally survey spectra of U-containing targets to search for characteristic UO bands were made.

In brief, we feel meaningful lifetime measurements were made in AlO, with the experimental approach being validated by checks on a C_2 Swan band and the Li 4133⁰Å line. Puzzling lifetime results from the Al lines and some other Li lines which originally led us to question the AlO results have been resolved to various extents.

So far no UO spectra have been observed in the near ultraviolet and visible, in keeping with the sparse literature on the subject. All of the above should be experimentally studied further.

A. AlO

Much of the project effort was devoted to the AlO and Al. While our results for AlO seem very reasonable, problems with the Al lines made the results originally suspect. Despite considerable progress near the project end, the lifetimes must be considered still preliminary. More work on this seems justified, even if AlO is assigned lower priority in DASA's future programs.

1. AlO Bands

AlO band spectra were recorded in the blowoff from ceramic Al_2O_3 targets in high vacuum. Al lines were also strong in these spectra, but the 0,0 band of the A-X transition selected for measurement was free of any spectral interference. The lifetime measured was 272 ± 14 nsec, at chamber pressures of 10^{-4} to 10^{-5} torr. The decay curves, corrected for noise in some cases, were typical of a single exponential.

This result is encouraging, but needs further confirmation. Agreement with the United Aircraft/AFWL theoretical calculation⁶ is good but probably fortuitous; their 230 nsec vs our 272 nsec. Their method of computation, while complex, is supported by excellent agreement with $\text{N}_2(1+)$ experimental data, while our experimental result is weakened by the behavior of the Al lines, but supported by C_2 and Li results. At present all we can say is that the 272 nsec measured lifetime probably represents an upper limit, and so a lower limit on the f-number and transition moment of AlO. For more on AlO recall our Section I-D-1 on AlO. See also Table 1 and Fig. 2.

One may wonder about the brevity of this AlO sub-section. This part of the program was straightforward, and there seemed little point in pursuing the matter further until expected routine calibration checks were made. As noted below, further work on AlO can be justified, using various geometries described. Eventually, lifetime measurements of several bands to study transition moment variation might be made.

2. Target Materials and Al Lines

Targets studied included Al_2O_3 hot-pressed ceramic wafers, Al_2O_3 powder in an epoxy matrix, Al wafers, Al folded foils, Al thin wires, and specially prepared Al deposited on quartz fibers. An additional extended test series was run using reduced laser power, a special focusing train to minimize the laser image spot size, and targets of Al films (60\AA to 200\AA thick) on glass. The considerable effort involved here was dictated by the unhappy discovery that routine checks on reported short-lived Al levels gave unexpected long lifetimes. The target materials and configurations were varied to study how these changed the observed lifetimes.

The two Al lines studied were those at 3944 and 3961\AA . Both originate from a common upper level ($4^2S_{1/2}$) having, according to NBS tabulations, a spontaneous lifetime of about 5 nsec. In checking this level lifetime experimentally we expected to encounter actual measured lifetimes of about 40 nsec, the present time resolution of our apparatus experimentally determined. However, the recorded lifetimes initially were in the 180-400 nsec range, and depend on the target material! Results from this puzzling earlier study are tabulated in Table II. See also Fig. 2. However, new geometry and excitation changed things drastically.

We describe the spectra instead of presenting photographs, since the Polaroid positives do not reproduce well. What is "observed" (recorded) is a presentation of spectral features as a function of wavelength vs intensity along the axis perpendicular to the target surface (slit is oriented perpendicular to the target surface). Most spectral features are confined to a geometric band defined by the target surface and the translational freezing radius; see Basov, et al.⁹ However, in some cases like Mg and Al, radiation from some very strong lines persist many mm away from the surface and outside the apparent freezing radius, at least, that radius defined by most of the observed emission. At the same time the bands, as from AlO, are confined largely within the freezing radius.

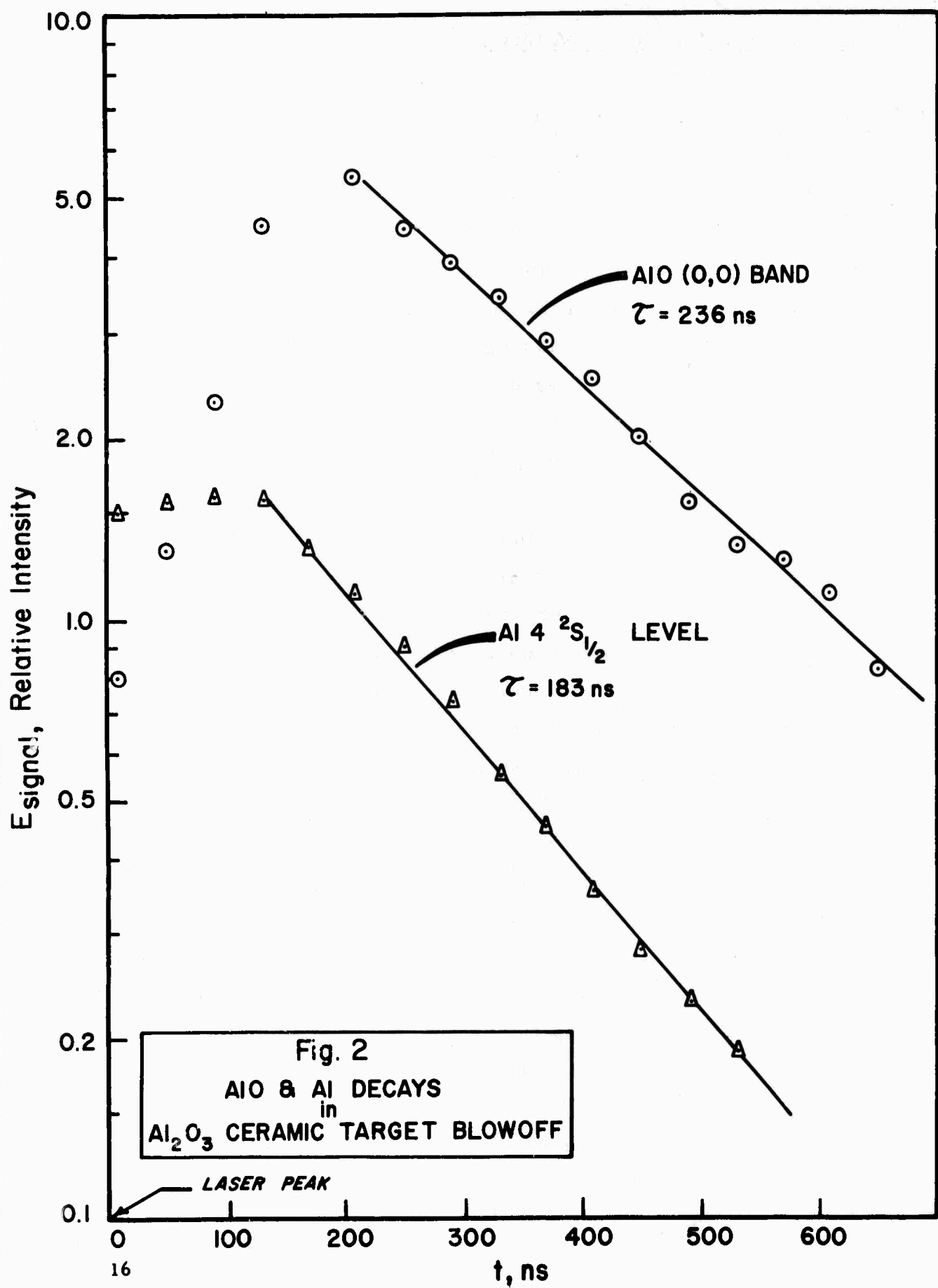


Table II

Measured Lifetimes of Al and AlO in Laser Blowoff

<u>Radiator</u>	<u>Target</u>	<u>τ, nsec</u>	<u>Remarks</u>
Al ^a	Al folded foil or solid plate	313 \pm 43	5 data curves
Al	Al ₂ O ₃ powder in epoxy matrix	402 \pm 158	3 data curves; Al signals weak, noisy
Al	Al film on quartz fiber	\sim 200?	Data in reduction needs more work
Al	Al ₂ O ₃ hot-pressed ceramic	223 \pm 26	3 data curves; more pending
AlO ^b	Al ₂ O ₃ hot-pressed ceramic	272 \pm 14	6 data points; more pending

a: $4^2S_{1/2}$ level, from $3961\overset{\circ}{\text{\AA}}$ line.

b: 0, 0 band.

One conjecture that might explain the anomalously long atomic Al lifetimes observed is that ionic Al might persist long after excited neutral Al has radiatively decayed; then recombination of $\text{Al}^+ + e$ to give excited Al may produce more Al emission and in the time scale observed. This must be investigated further.

Another possibility is cascading, which we rejected early, but must reconsider in any future study in view of the Li work done near the program end. In Al, the long decays recorded from the $4^2\text{S}_{\frac{1}{2}}$ (25348 cm^{-1}) level to the ground state were surmised to be a result of cascading from higher energy levels. Examination of an Al energy level diagram reveals that cascading from the $6^2\text{P}_{3/2, 1/2}$ metastable levels to the $4^2\text{S}_{\frac{1}{2}}$ level could indeed account for the long observed decays; however, the wavelengths that correspond to these transitions (5557 and 5558\AA) do not appear on any of our spectra, thus tentatively indicating that cascading through levels related to these lines is not occurring to any significant extent. On the other hand, there are many energy levels above the $4^2\text{S}_{\frac{1}{2}}$ level which can cascade into the $4^2\text{S}_{\frac{1}{2}}$ via a series of infrared transitions. Thus, it is impossible to rule out completely the possibility of cascading through lines beyond the spectral range we covered as the source of the long observed lifetimes.

An alternative explanation may be associated with the freezing radius, within which translational energy may provide re-excitation of decayed species and so yield long apparent lifetimes. As the radius increases (blowoff vapor expands) and the temperature drops, this re-excitation would tend to favor those species having shorter lifetimes and have the least effect on those having longer lifetimes. Thus, the distortion of the lifetimes recorded would be most pronounced early in time in the data records.

A reasonable support of this seems to rest in the experiments we did using the laser beam highly focused on the target to achieve a small heated area and very small or thin targets. The small diameter of the target area and thin aluminum coating should shorten the observed decays in two ways. Firstly, the smallness of the target area should contribute to

making the density of the blowoff fall off as the inverse cube of the blowoff radius, which is the optimum expansion geometry for reaching the freezing radius as quickly as possible. Secondly, the thinness of the aluminum coating should allow the entire surface coating to be completely vaporized, before the end of the laser pulse, thus preventing any further possible emission of excited metal atoms from volatilization after the end of the pulse.

Preliminary results showing shortened atomic aluminum decays with plated fibers and relatively large beam size were encouraging. The "one shot" nature of this type of experiment makes target alignment and correct adjustment of the photomultiplier gain extremely difficult tasks and one thus records many oscillograms with off scale traces. Then the "tight focus" on the 60\AA to 200\AA Al films was used. These tests showed results markedly different from the earlier experiments, the decays being intense peaks following the laser excitation pulse shape, followed by a long tail of negligible intensity. The long decay of the Al lines with considerable intensity encountered in earlier tests was gone. The spectra taken with this new geometry and thin samples showed a minimal freezing radius; the spectral features consisted of tiny spots with negligible height.

One critical experiment is missing as this report was readied for mailing: this is the measure of AlO lifetimes under these new excitation conditions!

B. LITHIUM STUDIES

The emission spectrum of atomic lithium (Li) in the laser blowoff was examined as a prelude to possible future excitation studies of LiO. Even more important are our preliminary lifetime measurements of various Li levels, since Li has a range of lifetimes that should be measurable with our laser blowoff apparatus, and hence apply to validation of our approach. Wiese, et al¹⁰ give transition probabilities for LiI; from these we calculated expected lifetimes of 14 to more than 1000 ns. See Tables III and IV.

Table III

Theoretical Level Lifetimes and Cascade Contributions in LiI

<u>Line λ, \AA</u>	<u>Transition</u>	<u>Cascade levels^a</u>	<u>τ, ns (calc.)</u>	<u>Cascade fraction^a</u>	<u>E_k, cm⁻¹</u>
3233	3p-2s	-	202(3p)	-	30925
		4s	57	0.43	35012
		5s	104	.29	38300
		6s	175	.25	39988
		3d	14	10^{-4}	31283
		4d	33	.23	36623
		5d	65	.22	39095
		6d	310	.60	40437
4133	5d-2p	-	65(5d)	-	39095
		6p	1010	0.14	40391
		6f	242	.17	[40439]
		5f	ignorable contrib. to 5d		39105
6104	3d-2p	-	14(3d)	-	31283
		4p	364	0.20	36470
		5p	549	.13	39016
		4f	72	.99 ⁺	36630
		5f	139	.64	39105
		6f	242	.51	[40439]

a: For example, the 3p level has a natural lifetime of 202 ns. The 4s level similarly has τ of 57 ns, and, thru ratio of A_{ki} , 0.43 of 4s population decays into the 3p state.

Table IV

Theoretical and Measured Level Lifetimes in LiI

<u>Level</u>	<u>Transition Measured</u>	<u>τ, ns (Theory)^a</u>	<u>τ, ns (Predicted Components)</u>		<u>τ, ns (Measured)^e</u>	
			<u>Major</u>	<u>Minor^f</u>	<u>Major</u>	<u>Minor</u>
3p	3p-2s (3233Å)	202 ^b [182] ^c	202	5 components less than 202 ns, and 1 of 310 ns.	70 and 349 to 130 and 413	
3d	3d-2p	14 ^b	(14) ^d	6 others in 72-549 ns range.	143	~1000
5d	5d-2p (4133Å)	65 ^b	65	2 others at 242 and 1010 ns.	91	~400

a: From reference 10; no cascading.

b: Theoretical accuracy claimed is 10%.

c: Experimental result of reference ¹¹ is 182 ± 6 ns.

d: Not expected in present experiment due to wide laser pulse.

e: Using simple assumption of only 2 exponentials in signal; further data and multiple exponential reduction needed.

f: See text and Table 3.

The observed Li spectra were weak but very clean, with several sharp lines displayed. Lifetime measurements were made at three line positions (3233, 4133, and 6104 Å), and on the weak continua at wavelengths adjacent to the 3233 Å and 6104 Å lines. However, first consider what should be expected in the level decay monitored at these wavelengths.

Let us predict what the observed decays of selected Li lines should be, accepting the tabulation of Wiese, et al. For example, take the 3233 Å line in emission (3p→2s levels involved). The spontaneous lifetime of the 3p level is readily evaluated, since it decays only via 3p-3s and 3p-2s, yielding the 26878 Å and 3233 Å lines, respectively. The corresponding theoretical Einstein coefficients A_{ki} are 3.77×10^6 and $1.17 \times 10^6 \text{ sec}^{-1}$, so the lifetime of the 3p level is 202 ns, with a 10% uncertainty.¹⁰ This is in good agreement with the experimental value 182 ± 6 ns reported by Isler, et al.,¹¹ who also gave a good review on this transition.

This level lifetime is well within our measurement capability, and the spectral accessibility and isolation of the 3233 Å line to monitor the level made this a priority line for check purposes, in our early planning. However, as described below, cascading processes make the expected decay complex and not too useful for testing a lifetime apparatus, if upper levels are appreciably populated as is evidently the case of the hot blowoff vapor. In retrospect, as noted later, the 4133 Å line and associated 5d level are "cleaner" for lifetime calibration. The results from the 5d level, while incomplete, are encouraging in validating our lifetime measurements approach.

However, the observed decays of 3p will probably reflect cascading effects if the 4s, 5s, 6s, 3d, 4d, 5d, and 6d levels are populated appreciably. All these levels decay to various extents through transitions to the 3p level. Taking into account such branching (e.g., 4s decays to 3p and also 2p), we see (Table 3) that, dependent on actual experimental populations, lifetimes of 33 to 310 ns can be reflected in the decay curve of 3p! Since 3p should decay according to a 202 ns lifetime, the states with shorter lifetimes

cascading into 3p will build up the 3p population until these states are depleted. Thus at early times 3p should appear to be decaying at a slower rate than predicted.

Now consider the 4133Å line of LiI, resulting in emission from the 5d→2p transition. As shown below, the situation is simpler than the 3233Å line and 3p level situation previously discussed. The spontaneous lifetime of 5d is shorter than the lifetimes of the levels feeding it, and those levels through branching contribute less to the population of the 5d, minimizing the cascading effect.

Proceeding as before, the 5d level decays by transitions to the 2p, 3p, 4p, 5p, and 4f levels. The sum of the A_{ki} is $1.54 \times 10^7 \text{ sec}^{-1}$, so the theoretical 5d lifetime is 65 ns (10% claimed uncertainty). The 6p, 5f, and 6f also can feed the 5d level, but the 5f population contribution is ignorable due to the small A_{ki} . The branching of 6p and 6f are such so that only 0.14 and 0.17, respectively, of those populations fall to the 5d level. The computed respective spontaneous lifetimes are 1.0 μs and 242 ns.

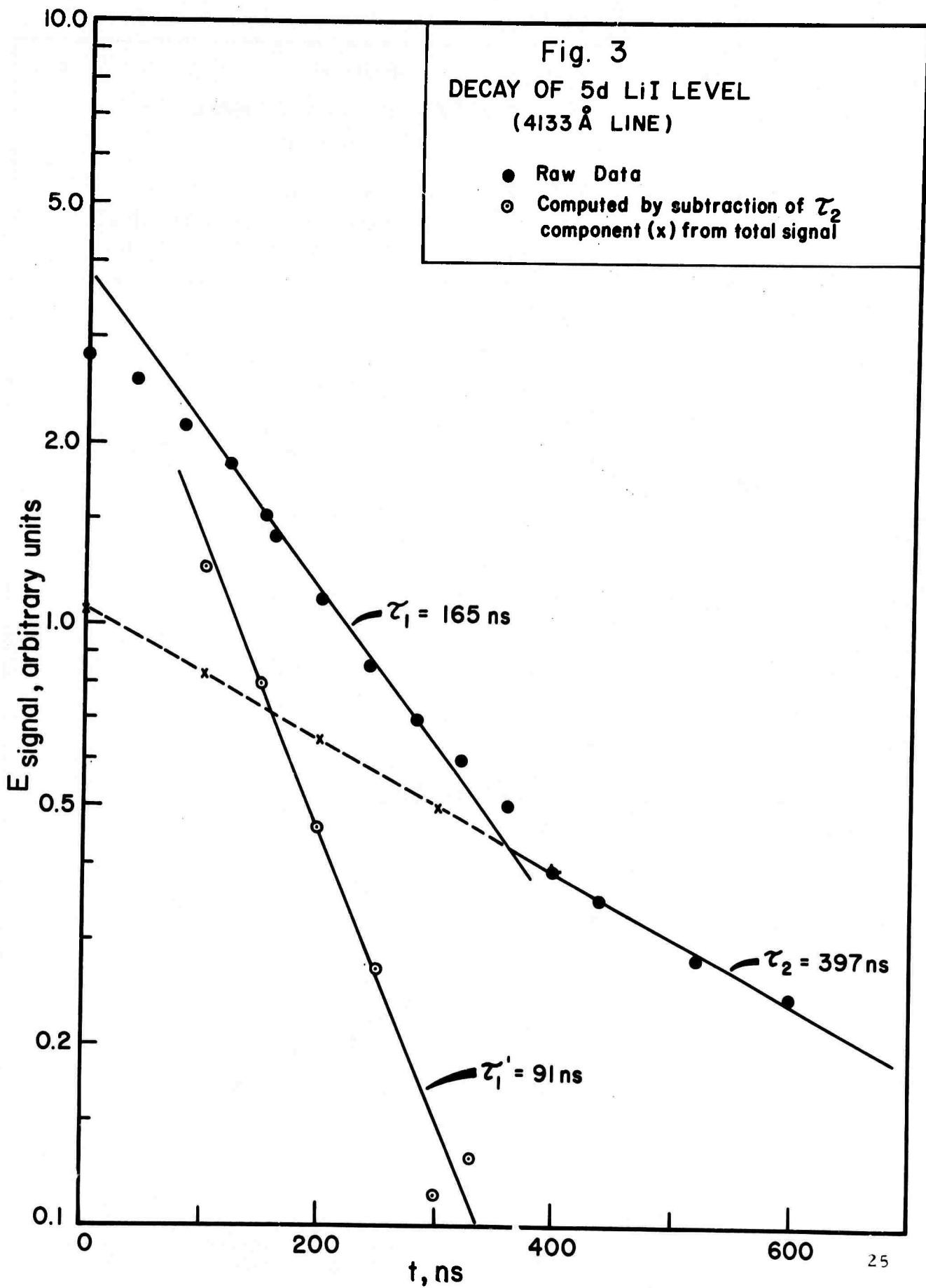
Thus, the predicted behavior of the intensity decay of the 4133Å line used to monitor the 5d level should follow a dominant contribution by a 65 ns decay, with distortion by smaller amplitude components with lifetimes of 242 nsec and 1.01 μsec.

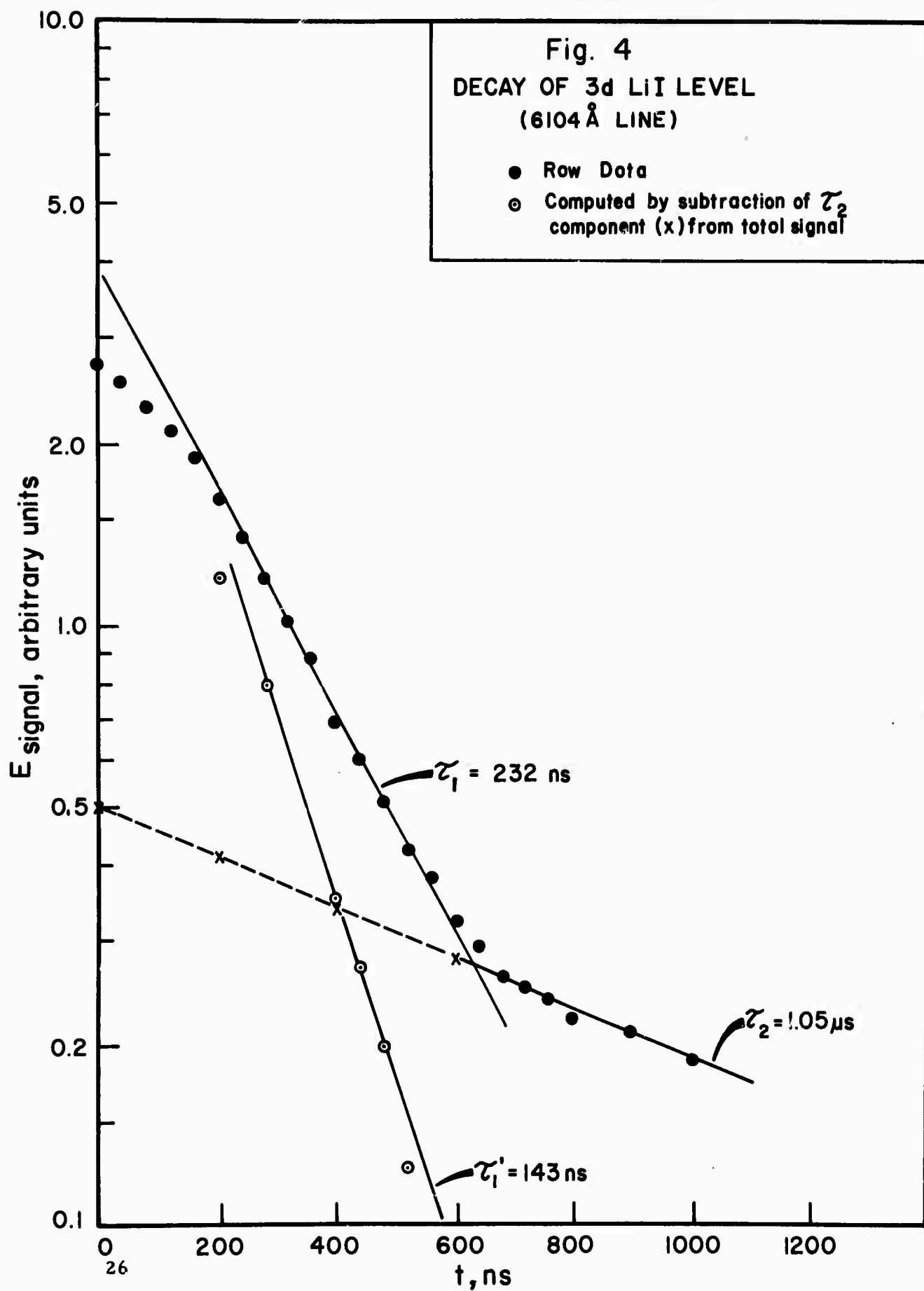
A typical experimental result is shown in Fig. 3. It is clearly not a single exponential. However, if one accepts the long term "tail" as an exponential with lifetime of 397 ns (from the plotted data) and removes this factor from the total signal amplitude, the remainder corresponds to another exponential with a lifetime of 91 ns. This is not too bad an agreement with the theoretical 65 ± 7 ns. Refinements (more detailed experimental data and subsequent computer analysis) to extract the 3 expected exponential terms should be done.

Proceeding as before we now examine the behavior of the 3d level, which decays almost entirely through the $3d \rightarrow 2p$ transition, producing the 6104\AA line. The computed 3d level lifetime is 14 ns. Likewise we deduce that the levels feeding the 3d level all have appreciably longer lifetimes. The data for the pertinent levels 4p, 5p, 4f, 5f and 6f are given in Table 3.

This is an interesting situation, especially experimentally, different from the other lines and levels considered earlier. This is because the primary datum sought, the 3d level lifetime said to be near 14 ns, is below the probable lifetime resolution of our apparatus, which is set primarily by the decay time of the laser pulse. Thus, in about the first 60 ns (4 times the 14 ns lifetime) after the peak of the laser excitation most of the 3d population produced during the laser pulse will have decayed. However, long after the excitation pulse is over there will still be 6104\AA radiation, since the 4f, 5f, etc. levels are still decaying into 3d. The important point is that the observed decay rate will be dictated by the slower cascading process, not the faster natural lifetime of 3d. Hence, as we presently operate, the 6104\AA decay curve should contain not a large factor in intensity due to 14 ns decay, but more important exponential factors involving lifetimes in the 72 to 549 ns range, with 72, 139, and 242 ns probably more important than 364 or 549 ns. The probable mix is difficult to estimate, unless thermal equilibrium and an initial vapor temperature are assumed.

Experimental decay measurements on the 6104\AA intensity history show reasonable agreement with expectation. Four shots each gave data like Fig. 4, with the uncorrected decay in the 100-500 ns range (after the laser pulse peak) behaving like an exponential with $\tau_1 = 231 \pm 4$ ns. Correction for the weak long "tails" having lifetimes τ_2 near $1.0 \mu\text{s}$ reduced the principal contributor to the intensity to one having a characteristic lifetime τ_1' of about 143 ns. This is admittedly simple-minded, since the experimental decay probably contains several exponentials.





This is the way the Li work stands, as experimental work was suspended to permit preparation of this draft of the contract final report. It is clear that more Li decays need to be predicted and measured, with emphasis on the long decays so as to allow better data reduction and analytical extraction of the various exponential components. This is best attempted via computer routines available to us. We intend to pursue this work during the period of review and correction of the draft report, and submit further correction pages if the results justify it.

C. FeO BANDS

The orange FeO system (see Appendix I) was produced at one atmosphere or air in the Q-switched laser blowoff. Fe_2O_3 in epoxy targets did not yield FeO spectra, but FeO powder in epoxy did. This band system is extremely feeble in comparison to other molecular spectra produced in this laboratory by the blowoff technique. The infrared spectrum of FeO excited in air is severely cluttered with intense iron lines appearing in second order, and conclusive identification of this system at first was not possible; however, the use of a sharp-cut filter to remove the second order lines alleviated this condition.

Utilization of oxygen at one atmosphere instead of air resulted in much stronger emission of the orange system of FeO. Many more band heads were observed and their identification was certain. The almost total suppression of atomic iron emission in this blowoff indicates that the atomic iron is probably reacting with the oxygen - a not so surprising result for blowoff produced at one atmosphere.

The FeO work was put aside in favor of the Al-AlO and other experiments. However, one significant result, based on the air vs O_2 atmospheres, suggested that similar studies with uranium might yield strong molecular spectra. This is discussed in part D of this section.

The orange and infrared systems of FeO were also recorded on Kodak type 1-N film. The latter system does not consist of sharp band heads, but

the spectra appeared to be of sufficient quality to warrant microdensitometry in the future. Various sources with many lines in the near infrared were investigated so as to provide a good calibration spectrum for accurate wavelength assignment of the band heads.

D. U AND UO: EMISSION FROM URANIUM-CONTAINING TARGETS

The spectra of the oxides of uranium (U) are of interest. The only published open literature on the subject in the visible and near infrared known to us are that of Gatterer et al.¹² (1957), and Mavrodineanu and Boiteux¹³ (1965). Gatterer et al said about their AC arc-produced spectra, in the 3900-8850Å range, using U rods in air, "There appears a very weak band structure besides the atomic lines, superimposed on a likewise heavy continuum." Also, "So far no analysis of the UO spectrum has been reported. The spectrum given here is mainly the arc spectrum of U, and the band structures that are seen are presumed to be due to the UO. The pronounced maxima of the continuum about 8200, 6000, and 4600Å might be real, and only partially due to the sensitizing characteristics of the L emulsion. The band structure is very weak and complicated. Most of the heads seem to be shaded to the violet, but no outstanding features can be observed under the present conditions. Measurement of these few features seemed to be of little value." The flame spectra discussed in reference 13 showed no bands.

There has been some conjecture that broad bands, from unpublished exploratory spectra, at 5300, 5650, and 6050Å might be attributed to some oxide of uranium. We sought these features, as well as those maxima given by Gatterer et al.

We did a survey of the emission spectra from various U-containing targets, described below, using the laser blowoff as the excitation. Survey spectra were taken to seek characteristic features which might be assigned to UO, UO₂, or their positive ions.

The 3100-8000Å region was briefly covered, but the near IR results were not promising and hence not followed. Most of the 110 spectra taken

were recorded in the 3100-6300 \AA spectral range. While the spectrograph used had greater range, the short wavelength limit was set by the absorption of a simple glass lens in the optical train. The long wavelength limit was dictated by the sensitivity limit of the Polaroid films employed. While a reciprocal dispersion of 10 \AA /mm is available and was used a few times, most data were taken at 23 \AA /mm.

In retrospect, and as we recommend for future work, the spectral studies should be repeated and extended, using glass negative plates to permit densitometry, since the Polaroid positive film used has limited dynamic range (about 25 from threshold to saturation). The survey should also be extended down to about 2300 \AA , a simple matter of using quartz in the output lens train, since the 2300-3100 \AA range may contain characteristic UO^+ spectra.

The targets were several. Metallic U was studied thru a depleted U metal slab (some oxide coating) and powdered U. Small UO_2 cylindrical reactor elements were held so as to be the target or were crushed and suspended by potting in BB2115 epoxy. Powdered U, and a mixture (equal volumes powdered) of U and UO_2 were also potted in the same epoxy.

The atmosphere surrounding the various targets was also varied. Spectra were taken in low (50 μ Hg pressure) and moderately high vacuum (10^{-5} torr), with air, or the following gases as the residual gas. Pure oxygen (O_2), hydrogen (H_2), helium (He), and nitrogen (N_2) atmospheres were used, usually in the 1 atmosphere to 10 torr range.

1. Calibration

A U-cathode hollow cathode lamp (Westinghouse-Jarrell-Ash Type 45447) was investigated as a source of U lines for calibration. Unfortunately this proved to be not very suitable for the purpose, due to the swamping of much of the U lines by the neon (Ne) used as the carrier gas in the lamp. Separate Ne and Hg lamps were used to sort out the complex lamp spectrum and to establish what were the few useful strong U lines; these are in the blue and near ultraviolet. However, one important result was that there

seemed to be no triplet of strong lines in the vicinity of 5570-5580Å that might be ascribed to the U line spectra or one of the spectral features mentioned by others.

2. General Nature of the Spectra

The spectra obtained were those of atomic U and continua of unknown origin. The U spectrum is complex; a tabulation of lines for a source of comparable temperature has been given by Meggers et al.¹⁴. Our observed intensity distributions, without correcting for film sensitization characteristics, show general agreement with Meggers et al. The lines are stronger in the ultraviolet, and the gross intensity falls off above 4800Å.

In the line spectra there are many triplets that give intensity peaks that could be mistaken for weak bands or heads. However, they can be associated with the line spectra. There was never a marked set of systematically emitted groups that could be clearly attributed to a band system.

All spectra considered, the U lines we observed seem to be characteristic of UI (e.g. the 5915Å line is moderately strong). Concerning the maxima¹² at 4600, 6000, and 8200Å, we saw little of interest at 4600Å except this is near the drop-off in intensity mentioned above. We cannot comment on the 8200Å maximum, since we did not cover it. The 6000Å feature¹² may correspond to that at 6050Å mentioned; we recorded a relatively strong triplet apparently lines, covering 5894-5976Å. There is another strong triplet in the 5568-5584Å range.

Details of specific target-atmosphere combinations are given in the following.

a. U metal (slab)

In low vacuum (50μ Hg of air) the U metal excited by the laser yielded sharp line spectra. At one atmosphere of air the emissions were stronger, with a quasi-continuum apparently due mostly to many smeared lines.

A more detailed series was run at lower powers (~1V, ND = 2.0), varying the pure O₂ atmosphere from 1 atmosphere to 10 torr. The emissions

were predominately smeared line "continua" at the higher pressures, with the lines becoming quite sharp at 10 torr. Almost identical results were obtained in a similar detailed test series with the test chamber gas changed to He. Similar spectra were obtained with the atmosphere changed to pure N_2 .

The above series with O_2 was run to test, naturally, if U atoms produced in the blowoff would react with the ambient gas to form any U oxides. The inert atmospheres were employed to test if the thin oxide coating of the U sample might be providing sufficient oxygen to allow production of UO or even oxidation of any UO formed in the blowoff to UO_2 . The spectra were quite indifferent to the ambient gases employed.

b. UO_2 (pellets) in O_2 atmosphere

Low power (0.1 volt, ND = 2.0): In this case epoxy was used to hold UO_2 reactor pellets to facilitate mounting, but the epoxy was not part of the active target surface. The atmosphere of pure O_2 was varied from 1 atmosphere down to 10 torr and then 0.1 torr. The spectra were unusually weak (compared to, for instance, U+ UO_2 mixture described elsewhere) and consisted of continua with the atomic lines difficult to see. However, at 0.1 torr the spectra increased drastically in intensity, with several features near 5890-5976Å becoming prominent. These broad lines (?) should be explored further, with glass plates and densitometry, since these features resemble poorly defined bands. At least, there is the greatest suggestion of band presence in the 5800-6300Å range, based on scrutiny of our numerous positive print (Polaroid) spectra.

c. UO_2 (in epoxy) in O_2 atmosphere

From targets containing crushed UO_2 suspended in epoxy and laser-excited in varying O_2 atmospheres down to 100 torr the spectra were a mixture of many lines on a strong continuum. At 10 torr and 0.04 torr the spectra were predominantly from U lines.

d. U+UO₂ (in epoxy) in O₂ atmosphere

A target of U powder and UO₂ powder mixed and then cast in epoxy showed unusual behavior when hit by the laser at low powers (peak 0.2V or less, ND = 1.0). The test series involved pure O₂ atmospheres from 760 torr down to high vacuum. All shots except those at high vacuum showed "sparks" emanating from the target (metallic U oxidizing ?). The spectra were marked by the absence of lines, being almost purely continua with only atomic lines superposed. These latter were the 2 Na yellow doublet (from the epoxy).

At higher powers (peak 1.0V, ND = 2.0), a factor of about 30 above the level that gave the continua described above, the spectra were the dense line spectra more usually observed.

e. U+UO₂ (in epoxy) - H₂ atmosphere

The previous results on the U+UO₂ target suggest that perhaps the hoped-for reducing reaction $U+UO_2 \rightarrow 2\ UO$ might be negated by either the U or any UO formed in the blowoff being converted by rapid oxidation to UO₂, by the excess ambient O₂. Thus, the chamber gas was changed to H₂.

The spectra were indeed different from the U+UO₂ in O₂ series, in that line spectra dominated at all pressures. Again, there are broad lines in the 5890-6300Å region that should be examined closer.

E. MISCELLANEOUS

One of us (TW) travelled to Palo Alto, California under this contract sponsorship to participate in the Sixth Meeting of the DASA/ARPA IR Working Group. The status of the Panametrics contract was presented.

While not a priority item in this contract, some small amount of time was spent on BaO calculations. BaO is of interest to DASA in Ba rocket releases, and also to Panametrics where laser blowoff studies were made earlier in a related contract. Using refined potential well constants based on this latter contract² (see also G. Wares' item in Acknowledgments),

refined realistic potential curves were constructed for the A and X states. Then for these potentials an 11×24 matrix ($v' = 0$ through 10; $v'' = 0$ through 23) of RKR Franck-Condon factors was computed. These were presented to ARPA in the January 1971 Monthly Progress Report. A detailed paper on BaO absolute intensity constants and the Morse and RKR $q_{v',v''}$ was submitted to JQSRT in March 1971, and has been accepted for publication.

While the results show no trends different from our^{2,16} Morse Franck-Condon factors or the RKR results of Zare¹⁵, some of the new numerical values are sufficiently different from the earlier results so that we recommend ours for any refined computations involving these $q_{v',v''}$. The major difference between ours and Zare's results rests on our use of microwave data for the rotational variation with v'' . However, we stress that there are no major differences in absolute intensity predictions or data reductions of the BaO A-X transition when using Morse in place of RKR constants.

IV. DISCUSSION

A. VALIDITY OF THE RESULTS

As stated in our original proposal, one major objective was the validation of the experimental approach, i. e., are molecular level lifetimes from the blowoff method significantly characteristic of the true spontaneous radiative lifetimes? In view of the experience with our calibration checks on C_2 Swan and the LiI 4133 $\overset{O}{\text{\AA}}$ line, and the molecules discussed below, we feel the AIO lifetime we report is meaningful. There is one remaining question: granted that we have been able, by experimental geometry changes, to reduce the A1 lifetimes to values limited by the apparatus time resolution, will the AIO lifetimes when measured under these new geometric changes remain unchanged? We expect this to be the case, but only further work can demonstrate this. Nevertheless, let us review the approach for some possible pitfalls, and at least consistency with other work. Consider the following questions and accompanying discussion.

1. Is the blowoff capable of yielding relatively long measured lifetimes?

Yes. Table 5 gives a summary of lifetimes measured in the blowoff for bands for 8 different band systems. Lifetimes from 5 different target materials were in the 135 to 900 nsec range, about the range we expect for AIO (excepting Ref. 5; recall Table 1 here).

2. Can meaningful time resolution be achieved using the blowoff? In other words, are measured lifetimes an indicator of level behavior due to the molecule, or swamped by the gross blowoff temperature-pressure history?

Meaningful time resolution is achievable. At least in the case of the C_2 Swan bands both Jeunehomme and Schwenker and Wentink, et al¹ found variation in lifetime with v' . Note Table 5. This lifetime variation

Table 5

Level Lifetimes From Laser Blowoff Experiments

<u>Molecule and Band System</u>	<u>v'</u>	<u>τ, nsec</u>	<u>Reference</u>
C ₂ Swan	0	324 \pm 28	1
	1	314 \pm 34	1
	2	290 \pm 23	1
	0	319 \pm 20	This work
C ₂ Deslandres-d' Azumbuja	0	343 \pm 14	1
	1	343 \pm 21	1
	2	360 \pm 20	1
C ₂ Fox-Herzberg		195	1
C ₂ Phillips		910	1
SiO Ultraviolet (A-X)		135	1
BaO (A-X)		400 \pm 100	2
VO (? ⁴ Σ - X ⁴ Σ)		\sim 410 \pm ?	2
AlO (A-X)		272 \pm 14 (preliminary)	This work

is consistent with that expected from transition moment variation studies. Also, our recent measurement, under similar blowoff vapor conditions, of different levels yielding various Lil lines showed quite different and expected decay behavior. This indicates we are testing discrete level behavior.

3. Have there been any independent checks on the same method?

Yes. In an effort to verify the correct operation of the experimental apparatus, and to investigate any possible deviations of our procedures from previously reported blowoff experiments it was decided that the lifetime data on the Swan system of C_2 previously reported¹ (Wentink, et al) should be redetermined. The Swan system of C_2 is easily produced in the blowoff at one atmosphere. At lower pressures it is not nearly so pronounced; however in comparison to other molecular spectra observed in this laboratory the Swan system is relatively bright with distinct band heads.

Lifetime data were recorded on the (0,0) band at $5165\overset{0}{\text{\AA}}$ with the pressure in the vacuum chamber less than 10^{-4} torr. The decays in general showed one peak with a long decay. A few of the photomultiplier traces showed a fast decaying peak about coincident with the laser pulse, but with an amplitude which was negligible in comparison to the slower decaying peak. The recorded lifetimes of the (0,0) band were between 298 and 348 nsec, yielding 319 ± 20 nsec, when the laser power was between 2.4 and 3.9 MW. These results are in good agreement with the work done at Avco.¹ Note Table 5.

4. Does quenching play a significant factor in the blowoff, at least in yielding low values of the lifetime?

Apparently not to any great extent. In fact, all measured lifetimes in C_2 Swan are longer than those deduced from other absolute intensity experiments. See reference 1 for more on this. Also, lifetimes from blowoff in SiO, VO, and BaO are in fair to good agreement with results from other methods like shock tubes.

5. Does further volatilization of the target surface after the laser heating pulse has ceased contribute to measured lifetimes longer than the true spontaneous lifetime?

This is an area of ignorance. The lifetimes we quote from this work were deduced from data starting about 100 to 200 nsec after the peak of the laser pulse. (These times involved careful corrections for delays of the photomultiplier electron transit time, cable delays, and even optical path delays.) In view of Ready's demonstration of rapid cooling of the surface after the laser pulse stops one would expect post-burst evaporation to be small. However, our (brief) experience with probable shortening of the measured lifetimes in Al when the plated fibers were tested indicates the contribution to the observed lifetimes when bulkier targets are used may not be negligible. This definitely needs further investigation.

V. RECOMMENDATIONS

We believe that the laser blowoff method should be studied and exploited further. Despite the problems encountered the method yields radiative lifetimes that are meaningful and characteristic of the species studied. While the limits of precision and accuracy in measured lifetimes need to be further defined, it is a powerful approach to the spectral and lifetime studies of refractory materials. Some specific problem areas suggested for future work are:

1. More analytical study of the behavior of the production of neutral particles (both atoms and molecules) near the blowoff threshold. Pressure and temperature histories and quenching effects should be stressed.
2. More measurements, still near threshold, with shorter laser pulse widths and decreased spot size (of the focused laser) to minimize geometric problems (especially the freezing radius).

This may require repetitive pulsing and signal integration because of the expected decreased emission per pulse. A N_2 laser of about 10 Kw peak power per pulse seems ideal to achieve this.

3. Continue spectral survey work related to the search for the UO. Extend the spectral range we covered. In particular, investigate the ultraviolet, say 2300 to 3100\AA using film, to check on possible band spectra of ionic uranium oxide, UO^+ .
4. In view of the fast response time of the radiative lifetime apparatus, in terms of expected reaction times, some exploration of the kinetics of U in various atmospheres should be made. While level spontaneous lifetimes probably would not be a product, the time history of lines, say a UI line, as a function of pressure and ambient gas may yield some measure of kinetic behavior.
Simultaneous histories of a UI and UII line could be useful, as might be simultaneous measure of the formation and decay of the observed continua relative to that of some selected U line. Of course, if definite spectral features of UO or UO^+ can be found, then similar but more elegant experiments are evident.
5. Investigate molecular studies in the near infrared (out to $1.0\ \mu$) that might be facilitated by the newly-available indium-doped gallium arsenide photocathode multipliers, considerable improvements over the S-1 photocathode multipliers in sensitivity and low noise.

VI. ACKNOWLEDGMENTS

In a complex and time-limited program of this type, and especially in these times of severe budgetary constraints, it is natural to seek assistance whenever expedient. We want to gratefully acknowledge the support of many others who helped in various ways.

First, our thanks to Dr. G. Wares, of AFCRL. An economic feature of the work is the fact that no capital funds for major equipment were requested. The necessary ruby laser and associated equipment were available at Panametrics. This "on-the-air" laser blowoff facility was assembled under AFCRL's contract with Panametrics, F19628-69-C-0172; OAR Project No. 8635, started February 1969 and presently scheduled to run through February 1971. The Contract Monitor is Dr. G. Wares. He verbally and enthusiastically agreed to use of the equipment for this present DASA/ARPA contract, on a noninterfering basis.

Dr. Russell Hill of Avco Corporation (Lowell) supplied high purity hot pressed target materials. Miss Sharon Dean and Dr. Jere Murray of the University of Alaska furthered the work by programming and machine computing. Similarly, Mr. Robert Spindler of Avco Corporation (Wilmington), made his computer programs available and carried out machine computations. Dr. Horace Furumoto and Mr. Harry Cecon of NASA-ERC, provided valuable advice, loaned equipment, and direct assistance in making the laser power calibration.

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APPENDIX I

Unclassified

(PRELIMINARY)

BAND SYSTEMS OF FeO

by Tunis Wentink, Jr.

December 1970

**PANAMETRICS, INC.
A Subsidiary of Esterline Corp.
Waltham, Massachusetts 02154
(617)-899-2719**

**Under Contract DASA-01-70-C-0155
ARPA Work Order 1433**

for

Defense Atomic Support Agency

and

**Advanced Research Projects Agency
Washington, D. C.**

ABSTRACT

Electronic band systems of FeO are reviewed. The ground electronic state vibrational transition $v = 0$ to 1 should be found at 11.48μ . This is based on refined data from the Orange bands.

The so-called D bands in the near infrared need further study, but appear to be due to a state 1.3 eV above, and connecting to, the ground state. This state has an ω near 670 cm^{-1} .

PRELIMINARY REVIEW OF FeO BANDS

This is a review as of December 1970 of the state of knowledge of electronic vibrational bands of FeO (iron oxide) and potential constants deduced from the measured bands.⁽¹⁻⁸⁾ It will be expanded from time to time, and revised as new inputs are obtained. It will be clear from the following that the status is not too good, and so this version must be considered preliminary. A preliminary energy level diagram showing the most probable arrangement of the various electronic states is presented in Fig. 1.

Ground State Constants

From various band systems terminating (in emission) in the ground state (X) the constants ω_e'' and $\omega_e x_e''$ have been calculated. From a quick scan of the literature one might judge that the numerical values seem to have been quite uncertain for a long time. However, the latest (1969) results⁽⁶⁾ we know about are quite consistent with results known as early as 1937.⁽²⁾ See Tables I and II. In particular, the 1966 data of Dhumwad and Narasimham⁽⁵⁾ (DN), when corrected for an apparently simple error (in ω_e''), are in good agreement with the 1969 results of Barrow and Senior.⁽⁶⁾

The ω_e'' and $\omega_e x_e''$ based on $\Delta G_{v''} + 1/2$ (or $\Delta G(v'')$) from the original data are also given in Table II. Unfortunately, these are mostly from band

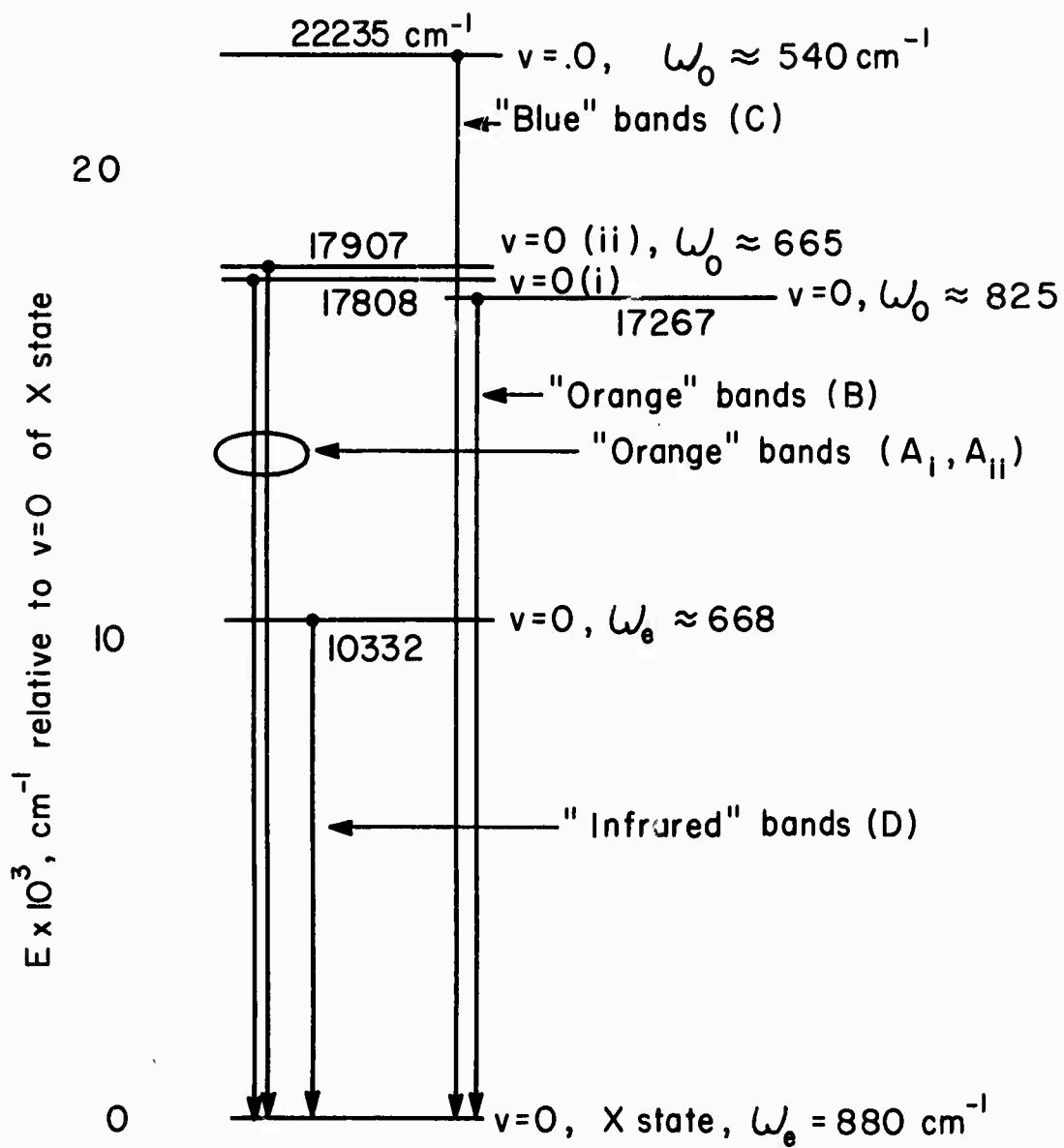


Figure 1. Sketch of FeO Electronic Energy Levels. (preliminary)

Table I

DESLANDRES TABLE AND CONSTANTS FOR FeO ORANGE BANDS

(A-X System)

For A_{ii} - X Bands*

$v' \backslash v''$	$\Delta G(v''=0)$		$\Delta G(v''=1)$		$\Delta G(v''=2)$		$\Delta G(v''=3)$	
	0	1	2	3	4			
0	5582.65	5868.00	6180.53	6524.15				
	17907.7	17036.9	16175.4	15323.4				
		870.8	861.5	852.0				
1	5382.1	5646.6	5934.8	(6250.0)	6596.6			
	18574.9	17704.9	16845.1	(15993.1)	15155.1			
		870.0	859.8	(852.0)	(838.0)			
$\Delta G(v'=0)$	667.2	668.0	669.7	669.7				

For A_i - X Bands

0	5614.0	5903.0	6218.9	6566.7				
	17807.7	16935.8	16075.6	15224.1				
		871.9	860.2	851.5				
1	5408.6	5678.9	5974.6	6295.9	6651.5			
	18483.9	17604.2	16732.9	15879.0	15030.1			
		879.7	871.3	853.9	848.9			
$\Delta G(v'=0)$	676.2	668.4	657.3	654.9				

* All data from band heads. Top entry in A_i⁰, second entry for head in cm⁻¹. All wavelengths from Pease and Gaydon (ref. 1) except for A_{ii}^{1, 3}, which we recomputed using $\Delta G(v'' = 2)$ of 852 cm⁻¹. Also the A_{ii}¹ bands from v' = 0 are from ref. 6, but agreeing closely with ref. 1 and ref. 5.

Table II
 $\Delta G_{v'' + 1/2}$ FOR GROUND ELECTRONIC STATE OF FeO

v''	Ref. # \rightarrow Date \rightarrow	1, 2 (1937)	1, 2 (1937)	5 (1966)	6 (1969)
0		870.8*	871.9**	870.8	871.27
		870.0*	879.7**	870.70 (0)+	
1		861.5	860.2	861.4	862.1
		859.8	871.3	---	
				861.90 (0)	
2		852.0	851.5	852.0	852.8
		----***	853.9	---	
				853.12 (0)	
3		---	---	---	843.5
			848.9	---	
ω_e''				880.2	880.53
				879.5 (0)	---
$\omega_e x_e''$				4.70	4.63
				4.40 (0)	

+ From band origins; all other entries from band heads.

* From $v' = 0$ of A_{ii} - X top entry, and $v' = 1$ bottom entry.

** From $v' = 0$ of A_i - X top entry, and $v' = 1$ bottom entry.

*** 923.1 cm^{-1} before correction of A_{ii} 1, 3 band as in Table 1.

heads and not from established band origins. One point we need to re-examine later is how valid are the vibrational potential constants based on the DN⁽⁵⁾ "origins," since their rotational analysis is probably wrong.⁽⁶⁾ However, the origins may still be correctly located.

Thus, for $\omega_e'' = 880.53 \text{ cm}^{-1}$ and $\omega_e x_e'' = 4.63 \text{ cm}^{-1}$, the $v = 0 \rightarrow 1$ transition for the ground state of FeO should be very near 871.27 cm^{-1} (vacuum) or $\lambda(\text{air}) = 11.47_5 \mu$. The 1-2 transition will be at 862.0 cm^{-1} (11.60μ), etc. Keep in mind these are based on electronic band head data, so the infrared band origins may be slightly different.

The A State

This state is poorly characterized. It is the upper state for the so-called Orange bands, $A \rightarrow X$. There are evidently levels with common v' split by about 100 cm^{-1} attributed to the A state, and designated by Gaydon⁽²⁾ as the A_{ii} and A_i bands. (Gatterer, et al⁽⁸⁾ call the A state by b_i or b_{ii} , and the B state by a). There are also levels relatively near ascribed to another state, the B, which give rise to the B-X system in emission. The splitting of the A state or at least the double heads of the A-X bands have not been explained. We put this off for explanation until later. However, in Table III the differences in the ii and i band heads for given v' , v'' are shown. For $v' = 0$, the quite good agreement in $\Delta\nu$ indicates a constant level splitting (or difference in head position for the ii and i bands) of 100 cm^{-1} . However, for $v' = 1$, the $\Delta\nu$ should also be constant with varying v'' but not necessarily the same as for $v' = 0$; the fact that it is not (91 to 125 cm^{-1}) probably means that the band head positions vary with the individual bands (and so with v'' for $v' > 0$).

The A state has either a very shallow potential well, or is perturbed in some way to cause predissociation. At least, only bands with $v' = 0$ and 1 are assigned. One result is that an anharmonic term ($\omega_e x_e'$) cannot be computed from the spectra, and only $\Delta G_{v'} + 1/2$ for $v' = 0$ can be deduced.

Table III

DIFFERENCES IN $A_{ii} - X$ and $A_i - X$ of FeO BAND HEADS

<u>v', v''</u>	<u>$\Delta\lambda, \text{\AA}$</u>	<u>$\Delta\nu, \text{cm}^{-1}$</u>
0, 0	31. 2	100.
0, 1	34. 9	101. 1
0, 2	38. 4	99. 8
0, 3	42. 6	99. 3
1, 0	26. 5	91. 0
1, 1	32. 3	100. 7
1, 2	39. 8	112. 3
1, 3	(44. 9)	(114. 1)
1, 4	54. 9	125. 0

From Gaydon's tabulation of band heads we computed it to be $666 \pm 2 \text{ cm}^{-1}$. This is quite different from the 770 cm^{-1} given by DN⁽⁵⁾, based on assignment of the 5614\AA band as the $A_{ii} 1,1$ band. Gaydon assigned this same band to $A_i 0,0$. We adopted for the A state tentative values of $\omega_e' = 674 \text{ cm}^{-1}$ and $\omega_e x_e = 4.0 \text{ cm}^{-1}$; these will be used for preliminary estimates of Franck-Condon factors we intend to compute later. Of course, these are subject to change due to any subsequent grating measurements.

The Infrared Bands

There are bands ranging from near 0.67 to 1.4μ attributed to a system called the D system by MR⁽⁴⁾ or the F-X system by BB.⁽⁷⁾ Our interest in this system is that if the lower state is the X state, as indicated by BB, the upper state is only about 1.3 eV above the ground state. See our analysis below. Thus, one can expect that with moderate thermal excitation, there will be many levels excited below a few eV. The numerous bands involved also follow the possibility of exciting (by decay) many vibrational levels in the ground electronic state; as shown later v'' of at least up to 8 are populated by radiative decay. The above is different from the analysis of MR, who proposed that their D system originated in the A state and terminated in a hitherto undiscovered lower electronically excited state about 1.6 eV above the ground state. As shown below we agree generally with BB and disagree with MR.

BB reported 63 band maxima measurements, and made vibrational assignments to 22 of their new bands, plus 3 to bands measured by MR. We reexamined the data of both, having refined values of $\Delta G(v'')$ from BS⁽⁶⁾ not available then to BB. Thus, the Deslandres table should be scrutinized more closely since these more accurate $\Delta G(v'')$ are available.

Using BS data, we computed $\Delta G(v'')$ values.

$$\Delta G(v'') = \Delta G_{v''} + 1/2$$

$v'' = 0$	871.3 cm ⁻¹
1	862.0
2	852.8
3	843.5
4	834.2
5	825.0
6	815.7
7	806.5
8	797.2

This assumes that $\omega_e y_e$ is ignorable, a necessary premise due to lack of data. Nevertheless, we can seek band head differences in the 800-871 cm⁻¹ and tentatively attribute these to $\Delta v'' = 1$, v' constant transitions.

Greater uncertainty is in the $\Delta G(v')$ characteristic of the upper state. BB says an average value of $\omega' = 654$ cm⁻¹ fits their data. A value of ω'_e near 670 cm⁻¹ seems to be a better value. We made a fit to and assignments of 53 bands, but hasten to add that this is still preliminary. While it is not reasonable to criticize any exploratory work like MR's or BB's, we do note the resolution was relatively poor (due to use of a prism) and the maxima do not necessarily represent band heads, let alone band origins, due to band overlap. MR's spectrograph had a dispersion of 50Å/mm or 139 cm⁻¹/mm at 6000Å, and so probably was poorer at longer wavelengths. BB's instrument (Perkin-Elmer 12C/dense flint prism) is described in terms of spectral bandwidth of 50 cm⁻¹ at 7150Å to 20 cm⁻¹ at 14,300Å (1.43μ). Thus, in taking band differences uncertainties of the order of the spectral bandwidths are not surprising. In any case we admit alternate vibrational assignments might be correct, and recommend some grating measurements be made to refine our analysis. Our results are in Table IV.

Our procedure involved trial acceptance of some band assignments, solving for ω_e, ω_x (assigning $\omega_e y_e = 0$), and T_e'' , and then predicting other

band head wave numbers. We used an IBM System 360/Model 40 computer and the Newton-Raphson iteration procedure to do this. The results below are based on input of 15 band assignments for the solution of the constants cited above, and the subsequent reasonable fit of 53 bands, of the total of 79 band maxima reported in the literature (excluding the orange bands) from 6700 to 13910 Å.

Using the above and $\omega_e'' = 880.5$ and $\omega_e x_e'' = 4.63$ (from BS), in

$$\begin{aligned} \nu_{v'} - \nu_{v''} = & T_e' - T_e'' + \omega_e' (v' + 1/2) - \omega_e x_e' (v' + 1/2)^2 \\ & - \omega_e'' (v'' + 1/2) + \omega_e x_e'' (v'' + 1/2)^2 \end{aligned} \quad (1)$$

we obtained $T_e' - T_e'' = 10437 \text{ cm}^{-1} (1.3 \text{ eV})$

$$\omega_e' = 670.2 \text{ cm}^{-1}$$

$$\omega_e x_e' = 1.99 \text{ cm}^{-1}$$

Table IV

COMPILATION OF RED AND INFRARED BANDS OF FeO

$\lambda, \text{\AA}$	ν, cm^{-1} (Meas, MR)	ν, cm^{-1} (Meas, BB)	Rel. Int. (BB)	ν, cm^{-1} (Calc, TW)	$\Delta(\text{m-c})$	$\nu' \nu''$ (BB)	$\nu' \nu''$ (TW)
6700	14920			14917	3		7, 0
6830	14637			14686	-49		8, 1
7022	14237			14273	-36		6, 0
--	---			(13824)			(8, 2)
7265	13761						
--	---			(13625)			(5, 0)
7428	13459			13401	58	6, 1	6, 1
7527	13282						
7690	13000			12973	27	4, 0	4, 0
7775	12858						
--	---			(12754)			(5, 1)
8112	12324	12313		12318	-1 (mean)	3, 0	3, 0
8230	12147			12128	19	4, 1	8, 4
--	---			(12102)			(4, 1)
8302	12042						
8320		12002	(2)	11992	10		13, 8
8369		11945	(3)	11930	15		9, 5
8414		11882	(4)	11892	-10	5, 2	5, 2
8474		11798	(3)	---			-
8515		11741	(3)	11738	3		10, 6
8578	11655	---		11659	-4		2, 0
8620		11598	(14)	11659	-61	2, 0	-
8742		11436	(6)	11447	-11	3, 1	3, 1
8790	11373	---		11371	2		12, 8
8808		11350	(14)				-
8844		11304	(14)	11294	10		8, 5
8864	11278	---					-
8899		11234	(14)	11240	-6		4, 2
8976		11138	(11)				-

Table IV(Cont'd)
 COMPILATION OF RED AND INFRARED BANDS OF FeO

$\lambda, \text{\AA}$	ν, cm^{-1} (Meas, MR)	ν, cm^{-1} (Meas, BB)	Rel. Int. (BB)	ν, cm^{-1} (Calc, TW)	$\Delta(\text{m-c})$	$\nu^I \nu^{II}$ (BB)	$\nu^I \nu^{II}$ (TW)
8998		11099	(10)	11105	-6		9, 6
9008	11000	---		10996	4		1, 0
9120	---	10962	(32)	10996	-34	1, 0	-
9200	10867			10843	24		6, 4
9258	10798	10807	(33)	10787	16		2, 1
9826		10766	(34)	10745	21	2, 1	11, 8
9333	10712	10708	(35)	---			-
9383		10655	(35)	10653	2		7, 5
9408	10626						-
9438		10593	(31)	10584	9		3, 2
9479		10547	(29)	10584	-37	3, 2	-
9676		10332	(38)	10329	3	0, 0	0, 0
9747		10257	(38)	10290	-43		9, 7?
9781		10221	(41)		26		
				10195			5, 4
9825		10175	(41)		-20		
9893		10105	(44)	10125	-20	1, 1	1, 1
9951		10046	(46)	10009	35		6, 5
10051		9947	(38)	9925	22		2, 2
10102		9896	(43)	9925	-29	2, 2	-
10149		9851	(39)	9828	23		7, 6
10208		9794	(35)	9786	8		12, 10
10257		9747	(30)	9732	15		3, 3
10380		9631	(28)	9653	-22	3, 3	8, 7
10533		9473	(54)	9458	15	0, 1	0, 1
10650		9387	(55)				-
10687		9355	(56)	9361	-6		5, 5
10737		9311	(53)	9319	-8		10, 9
10803		9254	(52)	9263	-9	1, 2	1, 2
10914		9160	(41)	9184	16		6, 6

Table IV(Cont'd)

COMPILATION OF RED AND INFRARED BANDS OF FeO

$\lambda, \text{\AA}$	ν, cm^{-1} (Meas, MR)	ν, cm^{-1} (Meas, BB)	Rel. Int. (BB)	ν, cm^{-1} (Calc, TW)	$\Delta(\text{m-c})$	$\nu' \nu''$ (BB)	$\nu' \nu''$ (TW)
11008		9082	(32)	9073	9		2, 3
11076		9026	(27)	9013	13	2, 3	7, 7,
11244		8891	(21)	8888	3		3, 4
11385		8781	(17)	8888	-107	3, 4	-
11466		8719	(17)	8710	9		4, 5 (14, 13)
11634		8593	(38)	8596	-3	0, 2	0, 2
11719		8531	(39)	8536 (8531)	-5 0		5, 6 (10, 10)
11773		8492	(42)				-
11856		8432	(44)	8410	22		1, 3
11916		8390	(48)	8382 (8366)	8	1, 3	11, 11 (6, 7)
12054		8294	(36)	--			-
12246		8164	(26)	8229	-65	2, 4	-
12404		8060	(17)	8054 (8050)	6		3, 5 (8, 9)
12911		7743	(12)	7743	0	0, 3	0, 3
12983		7700	(12)	7721	-21		5, 7
13065		7652	(13)	--			-
13238		7552	(22)	7566 (7562)	-14 (-10)	1, 4	1, 4 (6, 8)
13364		7481	(16)	7478	3		12, 13
13450		7433	(17)	7409	24		7, 9
13517		7396	(18)	7395	1		2, 5
13583		7360	(18)	7348	12		13, 14
13682		7307	(15)	7262		2, 5	-
13776		7257	(12)	7262	-5		8, 10
13849		7219	(9)	7229	-10		3, 6
13910		7187	(8)				-

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